Structural characteristics of positionally-disordered lattices: relation to the first sharp diffraction peak in glasses

J. K. Christie,* S. N. Taraskin, and S. R. Elliott

Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, CB2 1EW, UK

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Positional disorder has been introduced into the atomic structure of certain crystalline lattices, and the orientationally-averaged structure factor $S(k)$ and pair-correlation function $g(r)$ of these disordered lattices have been studied. Analytical expressions for $S(k)$ and $g(r)$ for Gaussian positional disorder in 2D and 3D are confirmed with precise numerical simulations. These analytic results also have a bearing on the unsolved Gauss circle problem in mathematics. As the positional disorder increases, high-k peaks in $S(k)$ are destroyed first, eventually leaving a single peak, that with the lowest-k value. The pair-correlation function for lattices with such high levels of positional disorder exhibits damped oscillations, with a period equal to the separation between the furthest-separated (lowest-k) lattice planes. The last surviving peak in $S(k)$ is, for example for silicon and silica, at a wavevector nearly identical to that of the experimentally-observed first sharp diffraction peak (FSDP) in the amorphous phases of those materials. Thus, for these amorphous materials at least, the FSDP can be regarded as arising from scattering from atomic configurations equivalent to the single family of positionally-disordered local Bragg planes having the furthest separation.

Medium-range order (MRO) in the structure of amorphous and liquid systems continues to attract a lot of attention.[1,2] The nature of the short-range order (SRO) in such systems is often accessible to diffraction or spectroscopic experiments, the physical interpretation of which, in the form of atom-atom pair-distribution functions, is clear.[3] The more subtle features which contribute to MRO, by contrast, are harder both to measure and to understand. Of particular interest is the so-called first sharp diffraction peak (FSDP), a characteristic feature of very many amorphous network materials.[4] This peak occurs in the structure factor at low values of scattering-wavevector transfer, k (= $|\mathbf{k}|$). The real-space information contained in the structure factor can be obtained via a Fourier transform, and so the FSDP at low k corresponds to atom-atom correlations at large distances; hence the presence of the FSDP is usually thought of as a signature of MRO.[1] Much effort has been expended in trying to deduce the real-space structural features which contribute to MRO and the FSDP in various amorphous systems;[4,5,6,7,8,9,10] explanations have been proposed, for example, based on the packing of voids in the material,[4,7] the existence of quasi-Bragg planes,[10] or other unknown effects.[9] Gaskell and Wallis[10] have stated that in many amorphous materials (although not all), the wavevector of the FSDP is close to the wavevector of a diffraction peak (the lowest) in a related crystalline phase, and thus, in real space, to a set of Bragg planes (with the largest interplanar spacing). They proposed that remnants of these lattice planes exist in the disordered phase, and that scattering from these planes causes the FSDP.

In this paper, we show that the wavevector of the FSDP in certain amorphous materials can be predicted from the lattice structure of their crystalline counterparts. Amorphous materials are positionally and topo-logically disordered; that is, the atoms have shifted from their crystalline positions. However, if the wavevector of the amorphous FSDP is close to that of the lowest peak in the crystalline structure factor[10] it is reasonable to assume that the MRO in the amorphous phase could contain structural configurations closely related to the crystal. The structure of amorphous materials was mimicked in this work by introducing positional disorder into the structure of certain lattices, and the behaviour of the structure factor and atomic-density pair-correlation function was investigated analytically and numerically.

Positional disorder was introduced into the crystal lattices by shifting each atom independently a random distance away from its crystalline position. In each of the x-, y- and z-directions, the shifts were randomly chosen from a Gaussian distribution centred on zero, independently of the shifts in the other directions. The half width σ of the Gaussian was thus a measure of the amount of positional disorder introduced. No restriction was placed on the closeness of approach of atoms (the results were not qualitatively different with a suitable cut-off).

If σ is small, the resulting disordered structure is rather like the original crystal; if σ is large, the atomic positions are located effectively randomly and little memory remains of the underlying lattice. Figure 1 shows the structure of the diamond lattice (Fig. 1a) as an increasing amount of positional disorder is introduced. The underlying lattice is still very clear at $\sigma = 0.1r_1$ (Fig. 1b), where r_1 is the crystalline nearest-neighbour distance. For $\sigma = 0.2r_1$ (Fig. 1c), some remnant of the {111} layers is still visible. Only faint vestiges of the crystal structure persist at $\sigma = 0.3r_1$ (Fig. 1d).

Gaussian positional disorder, as studied here, has a physical analogue: it corresponds to thermal motion of atoms about their crystalline positions.[11] In this work, the displacement of the atoms from their crystalline po-
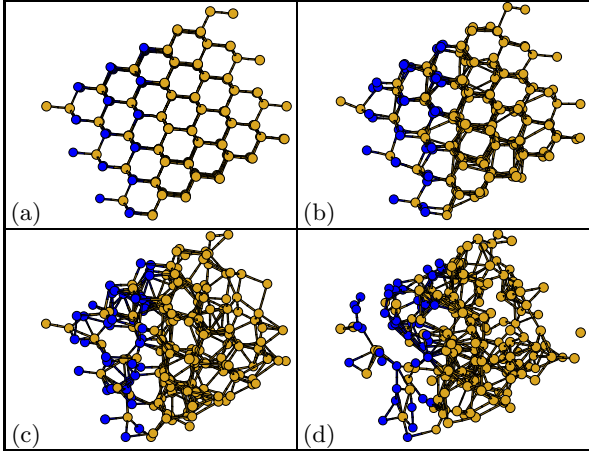
FIG. 1: (Colour online) Gaussian positional disorder in the diamond lattice with values of disorder parameter σ: (a) 0, (b) $0.1r_1$, (c) $0.2r_1$, (d) $0.3r_1$, where r_1 is the nearest-neighbour distance. All models have the same orientation. Atoms in three consecutive {111} lattice planes perpendicular to the page are darkened to show the gradual destruction of the lattice planes with increasing positional disorder.
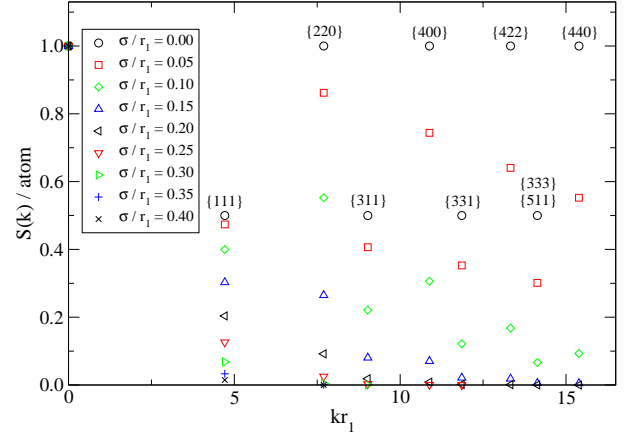

FIG. 2: (Colour online) Orientationally-averaged structure factor per atom, for Gaussian-positionally-disordered diamond lattices (with 97336 atoms) with different values of disorder parameter, σ, where r_1 is the nearest-neighbour crystalline distance. Only the lowest-k peak, at $kr_1 = 4.71$, contributes substantially for $\sigma \gtrsim 0.3r_1$.

sitions can far exceed that which would occur thermally in a real crystal, but the mathematical formalism is identical. In particular, the effect of thermal motion on the structure factor $S(\mathbf{k}) = 1 + \frac{1}{N}\sum_i\sum_{j\neq i}\exp(i\mathbf{k}.\mathbf{r}_{ij})$, where N is the number of atoms, and $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the position vector for the separation between atoms i and j, is well-known.[12,13] The crystalline Bragg peaks have a weight proportional to N;[14] thermal disorder reduces their weights by the Debye-Waller factor, $e^{-k^2\sigma^2}$ (without broadening the peaks) and a low-amplitude diffuse scattering intensity occurs. In terms of the (orientationally averaged) crystalline structure factor $S(k)^{cryst}$, the disordered structure factor for Gaussian positional disorder is given by:[12,13] $S(k) = 1 + e^{-k^2\sigma^2}(S(k)^{cryst} - 1)$. The Debye-Waller factor destroys the high-k peaks in the crystalline structure factor fastest as positional disorder increases (Fig. 2). It is clear that, as σ increases, there will be a range of disorder in which only one peak makes a substantial contribution to $S(k)$, the rest being negligible; this peak will be the crystalline peak at the lowest value of k. It is known[10] that the FSDP often has a very similar wavevector to that of the lowest-k peak in $S(k)^{cryst}$; here we see that this peak is the most resistant to positional disorder. The lowest-k peak in $S(k)$ corresponds to the set of Bragg planes which are furthest separated in real space; they are also the set of planes with the highest atomic density. Figure 2 shows the calculated $S(k)$ for positionally-disordered diamond lattices, with $N = 97336$ atoms, for various values of σ. The peaks decrease in height in very close accord with the theoretical Debye-Waller decrease. For $\sigma \gtrsim 0.3r_1$, only the {111} peak at $kr_1 = 4.71$ makes a substantial contribution.

The structure factor $S(k)$ is related by a Fourier trans-

form to the pair-correlation function $g(r)$ (the orientational average of $g(\mathbf{r}) = (N\rho_0)^{-1}\sum_i\sum_{j\neq i}\delta(\mathbf{r} - \mathbf{r}_{ij})$, where ρ_0 is the average density). Thus, the effect of positional disorder is to convolve the δ-function peaks in the crystalline $g(\mathbf{r})$ with the Fourier transform of the Debye-Waller factor. For Gaussian disorder, this gives:

$$g(\mathbf{r}) = \frac{1}{(2\sqrt{\pi})^d\sigma^d N\rho_0}\sum_i\sum_{j\neq i}\exp\{\frac{-(\mathbf{r}-\mathbf{r}_{ij})^2}{4\sigma^2}\}, \quad (1)$$

where d is the dimensionality of the system.

In principle, $g(r)$ can be evaluated by summing eq. 1 over all crystalline interatomic distances for a given lattice, and orientationally averaging the result. For the 2D square lattice with crystalline lattice positions $\mathbf{r}_i = n_x\hat{\mathbf{x}} + n_y\hat{\mathbf{y}}$, $g(\mathbf{r})$ in eq. 1 can be orientationally averaged to give:

$$g(r) = \frac{1}{4\pi\sigma^2\rho_0}\sum_{n_x,n_y=-\infty}^{\infty}\exp(-(r^2+n_x^2+n_y^2)/4\sigma^2)\times$$
$$I_0\left(\frac{r\sqrt{n_x^2+n_y^2}}{2\sigma^2}\right),(2)$$

where $I_0(z)$ is a modified Bessel function of the first kind. For the 3D simple cubic lattice, with crystalline lattice positions $\mathbf{r}_i = n_x\hat{\mathbf{x}} + n_y\hat{\mathbf{y}} + n_z\hat{\mathbf{z}}$, $g(r)$ is given by:

$$g(r) = \frac{1}{8\pi^{3/2}\sigma\rho_0 r}\times$$
$$\sum_{n_x,n_y,n_z=-\infty}^{\infty}\frac{e^{-(r-n)^2/4\sigma^2}-e^{-(r+n)^2/4\sigma^2}}{n}, \quad (3)$$

where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$, and the sums in eqs. 2,3 exclude the case where all indices n_i are zero simultaneously. It has not been possible to evaluate these sums analytically. In retrospect, this failure is unsurprising. More than 150 years ago, Gauss first posed what is known as the Gauss circle problem:[15] given a regular square lattice of points, and a circle of radius r centred on one of the points, how many lattice points lie within the circle? The exact answer remains unknown, despite much attention.[16] An exact expression for $g(r)$ with a width σ of zero would solve this problem. The equivalent problem is also unsolved in more than two dimensions.

Since it has not been possible to obtain $g(r)$ analytically, it was calculated numerically by simulating large ($\sim 10^5$ atoms) crystalline models of 2D square and 3D simple cubic (SC), face-centred cubic (FCC), body-centred cubic (BCC), diamond, and cristobalite (SiO$_2$) structures, which were then Gaussian positionally disordered with various values of σ. Periodic boundary conditions (PBCs) were used, and it was necessary to use large models in order to increase the number of allowed **k**-vectors, particularly for low k. PBCs also imply that $g(r)$ is not reliable for distances beyond half of the (cubic) box size L; data are not shown for values of $r > L/2$.

For the crystal (with $\sigma = 0$), $g(r)$ consists of a series of δ-functions at the various interatomic distances. For small σ (for $\sigma \lesssim 0.2r_1$ - not shown here), the δ-functions broaden into Gaussians[11] and merge, giving a complicated form. However, as σ is further increased, $g(r)$ takes on a simple oscillatory form with a *single* frequency, having an envelope that decays spatially as a power law (see Fig. 3). The 3D lattices were all found to have $g(r)$ decaying as r^{-1}, whilst the 2D square lattice was found to have $g(r)$ decaying as $r^{-1/2}$. The reason for this is clear: the 3D Gaussian $g(r)$ (eq. 3) has an explicit r^{-1} dependence, and the asymptotic behaviour of the modified Bessel function in the 2D $g(r)$ (eq. 2) has an $r^{-1/2}$ dependence. The simulated $g(r)$'s (Fig. 3) agree very closely with the theoretical expressions given by eqs. 2,3. If $g(r)$ consists of oscillations with a single significant frequency of period D, then there is only one significant peak in the structure factor $S(k)$, at a wavevector of $k_1 = 2\pi/D$. A heuristic argument for why only a single period is observed in the oscillatory behaviour of $g(r)$ at sufficiently large σ draws on the Rayleigh criterion for resolving overlapping broad peaks, such as those that occur in the sums of Gaussians in eqs. 2,3: two peaks are just resolvable when the full width of the peaks is comparable to their separation. Thus, for sufficiently large σ, only contributions from lattice planes with the *largest* separation combine to give resolvable oscillations in $g(r)$.

The periods of the oscillations, D, were extracted by assuming the empirical form $g(r) = 1 + Ar^{-1}\sin(k_1 r + \phi)$ for the 3D lattices, and $g(r) = 1 + Ar^{-1/2}\sin(k_1 r + \phi)$ for the square lattice, and performing a least-squares minimisation with respect to the variables A, k_1 and ϕ. Non-oscillatory data for $r < 2r_1$ were excluded from the fit. Averages were then taken over twenty realisations of
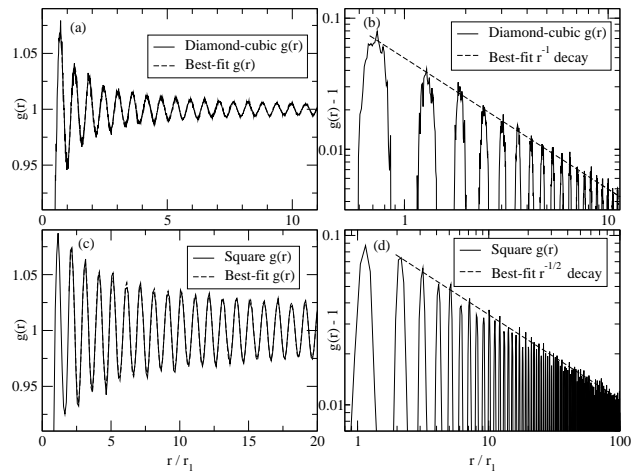

FIG. 3: (a) $g(r)$ for a Gaussian-positionally-disordered diamond lattice with disorder parameter $\sigma = 0.3r_1$ (solid), and the best-fit curve (dashed). (b) The same data plotted double-logarithmically with the best-fit r^{-1} decay envelope. (c) $g(r)$ for a Gaussian-positionally-disordered square lattice with $\sigma = 0.25r_1$ (solid), and the best-fit curve (dashed). (d) The same data plotted double-logarithmically with the best-fit $r^{-1/2}$ decay envelope. Both best-fit curves exclude the non-oscillatory data at low r.

each disordered model. For all the lattices studied, D is equal to the spacing between the furthest-separated lattice planes (see Table I). We conclude that these single-frequency oscillations in $g(r)$ correspond to the Fourier transform of the single remaining peak in $S(k)$.

We now show that positionally-disordered structures of appropriate crystal lattices can predict the position of the FSDP in various amorphous systems. Real amorphous materials show several peaks in $S(k)$, all of which comprise contributions from many interatomic distances. The corresponding $g(r)$ has several aperiodic peaks, and the single-period oscillation shown in Fig. 3 would modulate such peaks, giving rise to the FSDP. Recently, "time-frequency" wavelet-transform analysis has been applied to the study of disordered structures to elucidate the interatomic-distance contributions to different peaks, particularly the FSDP.[17,18,19] We show below that the FSDP in $S(k)$ for some amorphous materials could be due to scattering from structural configurations equivalent to the last surviving family of local, disordered Bragg planes in a positionally-disordered structure.

Silicon crystallises in the diamond structure, and its amorphous form has been well studied as a canonical example of a topologically-disordered solid.[3] It also exhibits a strong FSDP at $k_1 = 2.00$Å^{-1}.[20] From Table I, the period of the last surviving extended-range oscillations in $g(r)$ for the positionally-disordered diamond lattice is the distance between successive {111} planes, i.e. the apex–basal-plane distance in an SiSi$_4$ tetrahedron, $D_{111} = \frac{4}{3}r_1$. In crystalline silicon, $r_1 = 2.35$Å,[21] corre-

Lattice	Furthest planes	Interplanar distance	Period of oscillations, D
SC	[100]	r_1	$(1.0000 \pm 0.0003)\,r_1$ for $\sigma = 0.25r_1$
FCC	[111]	$\sqrt{\frac{2}{3}}r_1 = 0.8165r_1$	$(0.8167 \pm 0.0001)\,r_1$ for $\sigma = 0.25r_1$
BCC	[110]	$\sqrt{\frac{2}{3}}r_1 = 0.8165r_1$	$(0.8165 \pm 0.0001)\,r_1$ for $\sigma = 0.25r_1$
Diamond	[111]	$\frac{4}{3}r_1 = 1.3333r_1$	$(1.3333 \pm 0.0001)\,r_1$ for $\sigma = 0.35r_1$
Square	[10]	r_1	$(0.99993 \pm 0.00001)\,r_1$ for $\sigma = 0.3r_1$

TABLE I: Families of lattice planes with the largest interplanar distance for certain crystal structures; r_1 is the nearest-neighbour distance in each case. For the values of disorder parameter, σ, given, $g(r)$ consists of oscillations having only a single frequency, the periods of which, D, were found from a best-fit procedure, as described in the text.

sponding to an oscillation with a period of $D = 3.13$Å, and hence $k_1 = 2\pi/3.13$Å$= 2.01$Å^{-1}, in excellent agreement with the experimental value above.[20]

The FSDP is often observed in AX_2-type glasses,[1,4] the most well-known example being vitreous silica, v-SiO_2. A crystalline counterpart of v-SiO_2 is the tetragonal α-cristobalite structure.[22] Real v-SiO_2 is known[1] to consist of fairly ordered SiO_4 tetrahedra, linked in a corner-sharing manner in a disordered network; we made no attempt to keep the tetrahedra ordered, and Gaussian disordered the atomic positions of cristobalite without restriction. Hence, these models are not a particularly good representation of real v-SiO_2. Nevertheless, single-frequency extended-range oscillations in $g(r)$ were found in positionally-disordered cristobalite structures for $0.35 \lesssim \sigma/r_1 \lesssim 0.6$. The period of this oscillation is $D \simeq 4.07$Å, corresponding to a peak in $S(k)$ at $k_1 \simeq 1.54$Å^{-1}, in very good agreement with the experimental value of the FSDP wavevector at $k_1 = 1.52$Å^{-1}.[23]

In conclusion, Gaussian positional disorder has been introduced into a variety of crystalline lattices, specifically, the 3D diamond, FCC, BCC, SC and the 2D square lattices, as well as the cristobalite crystalline polymorph of silica. As this positional disorder increases, the high-k Bragg peaks in the structure factor are destroyed first, eventually leaving only the lowest-k peak in $S(k)$. Examination of the orientationally-averaged real-space pair-correlation function of such disordered structures shows power-law-damped, single-frequency, extended-range oscillations, with a period, D, equal to the spacing between the most distant (most areally dense) lattice planes. This period is equal to $D = 2\pi/k_1$, where k_1 is the wavevector of the first peak in the structure factor. The atomic positions of crystalline counterparts of silicon and silica have been disordered. The wavevector of the FSDP in real amorphous silicon and in vitreous silica, is nearly identical to that of the lowest-k peak in the structure factor of the positionally-disordered crystalline counterparts, and hence at sufficiently large distances from an arbitrary origin atom, the atomic structure of a topologically-disordered amorphous material appears to be similar to that of the corresponding positionally-disordered crystal.

* Electronic address: jkc25@cam.ac.uk
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